



Analysis of good practices, barriers and drivers for ELTs pyrolysis industrial application



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ABSTRACT

Boosting of eco-innovative solutions for End of Life Tyres (ELTs) management, under the principles of the EU Resource Efficiency Roadmap and the Waste Framework Directive, can not only diminish the environmental hazards and the consequent societal cost, but also result to the establishment of a novel perception regarding ELTs; thus, a valuable stock of resources that can be exploited. Despite the extensive scientific research of the previous years on ELTs depolymerisation via pyrolysis highlighting its eco-innovative characteristics, the use of pyrolysis to process scrap tyres has not yet achieved a broad commercial success, with economic viability and product standardization to constitute the primary impediments. More specifically, pyrolysis was not applied to an extensive industrial scale so far, due to deficient market analysis, legislative barriers, economic instability and sometimes public acceptance. All the above issues are addressed by the present study. Modifications on current EU legislation can prevent or reduce delays or derailment of efforts on pyrolysis, through its differentiation from incineration. The attainment of economic viability could be realized through the valorization of the pyrolytic char towards activated carbon production for environmental depollution applications; needless to say, the penetration on niche and well-organised markets is more than essential.

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1. Introduction

Recent statistical data on tyres production in Europe reveal market's struggle to recover from financial crisis's outcomes. More specifically, despite the intense increase on tyre production noticed in 2010 (26% growth rate compared to 2009), the maximum production of all time still has not been overcome (in 2007 more than 5.1 million tonnes of tyres were produced). In turn, these variations on tyre production strongly affect the generation of waste tyres or End of Life Tyres (ELTs); in Europe, a typical annual generation of ELTs exceeds 3 million tonnes. This vast amount of generated wastes require additional cost to societies for their effective management, since ELTs were proved responsible for several possible environmental hazards (ETRA, 2013a,b).

Current European policy for ELTs management thrusts towards sustainability and recovery of resources, thus promoting the development of innovative methodologies, which provide a wide variety of marketable materials and products (ETRA, 2014). Based on statistical data, the most preferred option (40%) for ELTs management

aims to material recovery through physical shredding, or granulation/crumbing operations (ETRA, 2014).

On the other hand, shredded tyres are the main constituent of tyre-derived fuel (TDF). ELTs can be a fuel substitute; in most cases they are mixed with coal or wood and burned in cement kilns, power plants, or paper mills (energy recovery is the second most widely used option, utilizing up to 38% of ELTs). Apart from zinc emissions, the use of TDF as a fuel in a well-designed, well-operated and well-maintained combustion device, does not generate emissions highly different, as compared to those originated from conventional fossil fuels use (E.P.A., 1997).

Thermal treatment technologies such as gasification, plasma gasification and pyrolysis were proved of limited applicability, due not only to their complexity as processes and to their inability in managing a variety of waste streams that require pre-treatment, but also to their lower net-energy recovery. The combination of applied technological advances with a reconceptualization of methods towards materials and energy recovery, aims to establish new generation technologies, treatments and end-products (ETRA, 2014).

So far, depolymerisation for energy and materials recovery was performed in batch or continuous processes, either at atmospheric pressure or under vacuum. However integrated ELTs management

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systems should consider recovery of steel, and fibers along with gas, liquid and solid products production. Based on market's needs, several issues need to be addressed so as to establish economically viable outlets (ETRA, 2014).

EU has co-financed pyrolysis demonstration projects, aimed at supporting initiatives which encompass technological development, while triggering the establishment of supply chains for these waste materials. Over the last two decades, plants have been built at pilot and demonstration scale, as a large number of developers and investors were intrigued by the potentials of tyre recycling market. Few examples of ELTs pyrolysis facilities were able to achieve and sustain a long term operation and even less, managed to produce a detailed and fully specified commercial product. There are thus still impediments in ELTs pyrolysis commercial implementation. However, the industry continues to evolve and facilities are being proposed, developed and commissioned. The materials produced from these operations, provided they match quality standards, will no longer be considered as wastes (TRA, 2012; WRAP, 2009). On the contrary, steps to commercialize ELTs pyrolysis plants have already emerged mainly aiming to liquid fuel production, though (Islam et al., 2013). As more actual performance data is generated, it has become clear that pyrolysis process is facing non-technological barriers that hinder its large scale market uptake in most EU Member States; if the limitations of these approaches are resolved, pyrolysis technology viability can be secured.

The present study aims to identify barriers which have impeded the development of “Depolymerisation” as a “Best Known Method” for ELTs, providing also a detailed analysis of the economic and non-technical roadblocks. Moreover, through suggested good practices, the identification of issues and practices which could lead to a broader acceptance of pyrolysis in the ELTs recycling sector, is presented. Stakeholders may find this contextual information useful for probable investment on pyrolysis. The ultimate aim of this study was to provide recommendations on an alternative ELTs management, through material and energy recovery.

2. Conceptual approach

End-of-Life Tyres (ELTs) are defined as tyres which can no longer be used on vehicles, including passenger cars, trucks, airplanes and motorcycle tyres (after retreading or regrooving). ELTs are classified as non-hazardous waste (75/442/EEC amended by Directive 91/156/EC). ELTs form and characteristics, permit their valorisation either for material (shredding, grinding) or energy (cement kiln, power plants and electric arc furnaces) recovery (ETMA, 2009).

The concept of pyrolytic processing of waste tyres, is proposed in this study as a thermal practice for energy and high added value materials (activated carbons for adsorption applications) production. The reasons for this choice are based on:

- the constantly expanding worldwide market of activated carbons (Freedonia-Study, 2013),
- the high selling prices that commercial activated carbons can mark, depending on the proposed application (Freedonia-Study, 2013),
- the efficiency of ELTs based activated carbons in water depollution applications including pesticides, heavy metal and dye removal from liquid effluents and also, in gas storage and gas purification (from waste to energy plants) applications (Chan et al., 2012; Gupta et al., 2013, 2014; Mui et al., 2010; Skodras et al., 2007),
- concerning energy balance, depolymerisation via pyrolysis is an endothermic process. ELTs energy content can be partially recovered by pyrolysis and reused to cover plant's energy needs (Antoniou and Zabaniotou, 2013),

- results from published studies indicated that positive economic indicators will be obtained, only when depolymerisation process goes beyond primary products and integrates additional stages, so as to obtain energy and/or products of higher added value (Choi et al., 2014; Islam et al., 2011).

The successful implementation of ELTs pyrolysis, strongly depends on technology (type of reactor) applied, economics, reliability of supply, management structure, as well as on standards and restrictions on ELTs use. Additionally, solid product's characteristics are also a matter of great importance, regarding economic feasibility of an ELTs pyrolysis plant. Through this study, a dual hybrid system for processing scrap tyres into high added value carbonaceous products (activated carbons) is proposed. More specifically, char can be upgraded in a closed-loop activation step to activated carbons, which exhibit similar structural and surface characteristics to commercial ones. The proposed process yields also substantial quantities of gaseous and liquid products, which by further processing can become value-added fuels.

Shredded tyres are depolymerised using indirectly heated reactors to isolate and reclaim pyrolysis char, steel cords, oils and gases. The non-condensable gas can be used as fuel for the dual hybrid system. The produced oil can be used domestically, as fuel for electricity generation but also be sold in designated markets. The recovered steel can also be sold directly, to niche but existing markets.

3. Suggested Good Practices (SGP)

Based on a running EU funded project (DEPOTEC project -LIFE10 ENV/IE/000695) (DEPOTEC, 2011–2014) which aims at the investigation of ELTs pyrolysis as a sustainable management option, suggested good practices on ELTs pyrolysis with broader acceptance and thus implementation, are listed below.

Under the general suggested good practice, the whole process was split in 5 different sections (Fig. 1), sub-good practices (SGP):

1. Pre-treatment of raw materials.
2. Slow pyrolysis.
3. Activation of the solid product.
4. Collection of end-products.
5. Energy recycling in the plant for reduction of plant's energy needs.

3.1. SGP I: pre-treat raw materials

Pre-treatment of raw material (ELTs) refers mostly to shredding and steel cords removal. The main feedstock preparation equipment available can be split into ambient and cryogenic processing. The choice of technology would depend upon the market for the end product.

Ambient processing of tyres is the most commonly used method for size reduction. The production of sized reduced rubber materials is governed by PAS107 (TRA, 2012) and the WRAP Protocol for Tyre Derived Materials within UK (WRAP, 2009). Through PAS107 and WRAP, specifications for producing grades of size-reduced rubber are provided, while minimum qualitative characteristics for potential customers are ensured. Every size-reduced material covered by PAS, is classified as waste until incorporated into an end use application (PAS-107, 2012). Handling and storage of these materials must comply with the regulations stemming from the Waste Framework Directive (WFD, 2008).

According to the common practice of ambient processing, used tyres are fed into a shredding machine (either manually, or using a conveyor system) which reduces the tyre size by slicing, using in

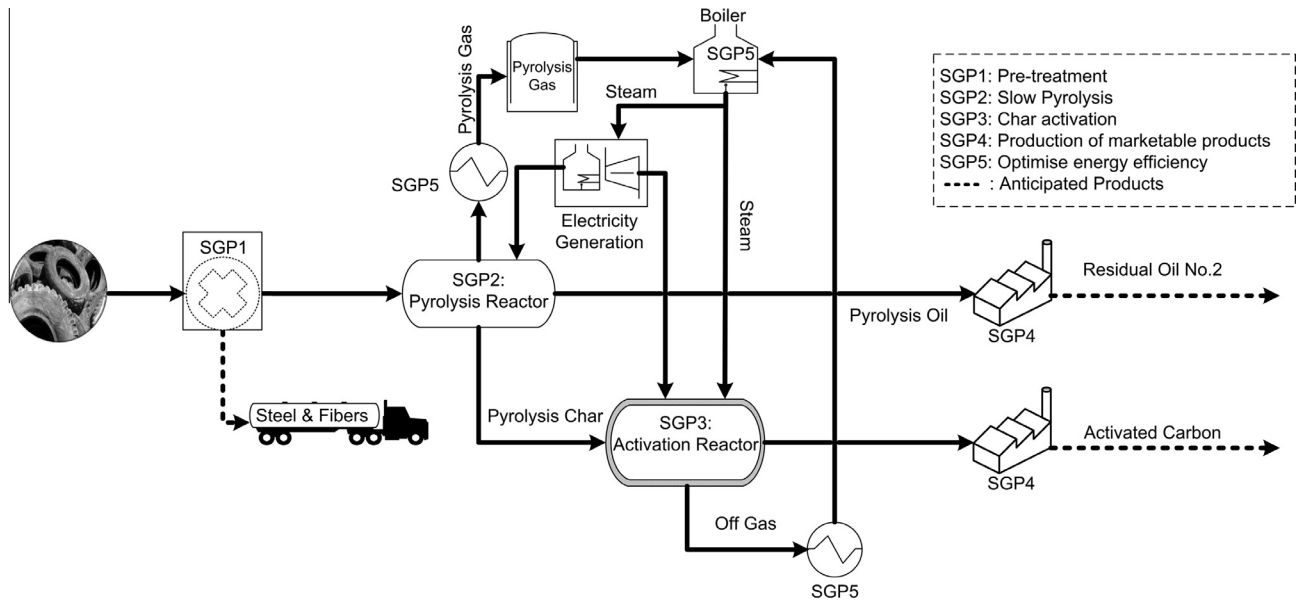


Fig. 1. Conceptual approach an integrated ELTs pyrolysis process with activated carbons production.

most cases fixed rather than floating knives. The produced cuts and shreds or 'rubber shreds' size ranges between 50 and 300 mm. Following, tyre shreds are granulated and magnetically separated; resulting to steel cord-free rubber chips (10–50 mm) (Fig. 2). In most cases, over 99% by weight of the metal is removed; thus, the rubber material can be sold into defined and designated markets. At this stage, granulation (between 2 and 4 mm), pulverization (between 0.8 and 2.5 mm) and micronization (less than 0.8 mm) can also be achieved (Uruburu et al., 2013). For even smaller particles, micro-milling in a wet medium is proposed; however the process's environmental footprint is high, since not only additional energy is required, but a possible leaching of organics and metals may occur (WRAP, 2009).

Rubber particles and dust extraction systems have to be employed at each grinding stage using a suitable filtration system. The collected material can be further reworked into finer grades. There may be additional process stages required, depending on the end-product size, quality and quantity requirements. The received products are expected to exhibit high surface area values. This is a useful characteristic in case of construction and engineering applications, requiring improved bonding with other additives and aggregates. Finally, the ambient grinding of ELTs provides a wider range of products despite the large maintenance cost associated with keeping the cutting equipment in a 'sharp and operational' condition; inevitably, its condition will degrade over time with increasing throughput. Technical and economic analyses were

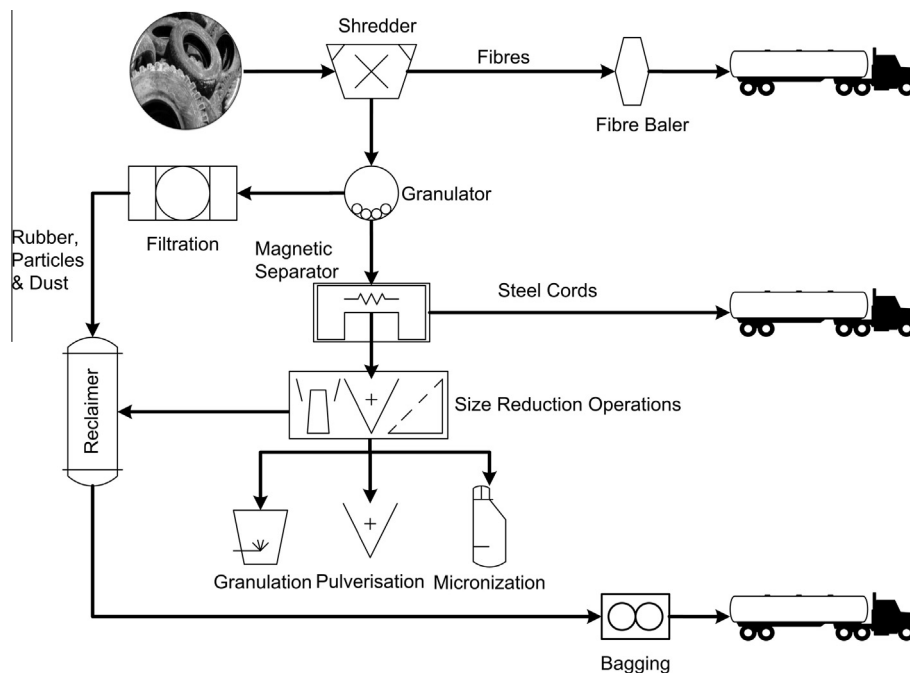


Fig. 2. Four stages of ambient grinding process of ELTs. (A) Primary shredding. (B) Production of granulated particles. (C) Classification of products. (D) Packaging and transportation.

conducted for various shredding suppliers. However, each proposed equipment assessment was based on the end-application of the rubber product obtained, such as tyre-derived-fuel (TDF), equestrian chip, shredders, powder and rubber granulates.

Cryogenic grinding is taking place under low temperature (-190°C) by using liquid nitrogen, producing fragile and low-elasticity particles. Most rubber compounds freeze at their glass transition temperature (-62°C). The derived products are grounded, milled and dried. At this stage rubber, steel and fibers can be exported (Sienkiewicz et al., 2012; Uruburu et al., 2013). The end product is purer but with higher humidity, (about 12–15% of the mass) with particle size ranging from $125\text{ }\mu\text{m}$ to $600\text{ }\mu\text{m}$ (WRAP, 2009), compared to that of ambient processing. Additionally, process's operational cost, energy needs and environmental impact are high, thus not characterizing cryogenic grinding as an optimum solution (Clauzade et al., 2010).

The fact that cryogenic grinding is considered the worst option among mechanical pulverisation process, waste to energy and the substitution of conventional fuel in the cement clink process was proved by an LCA study using Eco-indicator'95 environmental indicators. In the same study, for the the production of 1 t of pulverized tyres with particle size $<2\text{ mm}$, 2956 KW are required in the case of cryogenic process, whereas only 1380 KW are required for the case of ambient process used (Corti and Lombardi, 2004).

3.2. SGP II: operate slow pyrolysis in a rotary kiln at 550°C

Pyrolysis is the thermal decomposition of organic materials in the absence of oxygen, cracking them down to simpler organic compounds. It relies on the addition of heat to break chemical bonds, providing a mechanism by which, organics decompose and vaporize (Antoniou et al., 2012). ELTs pyrolysis process was mostly performed within a temperature range of $400\text{--}600^{\circ}\text{C}$; however certain experimental set ups require elevated operating temperatures, even exceeding 1000°C (Fabbri and Vassura, 2006; Huang and Tang, 2009). According to Martínez et al., 2013b, during pyrolysis the separation of carbon black from tyres is achieved, along with the release of volatiles (condensable and non-condensable compounds).

Pyrolysis can be classified as atmospheric, vacuum, catalytic, fast or slow, depending on the operation parameters applied (Antoniou and Zabaniotou, 2013; Martínez et al., 2013b; Williams, 2013). Through this process, products with high energetic content, as well as valuable char can also be obtained, after the necessary pretreatment (EU-BREF, 2006).

Slow pyrolysis plants can be designed to operate either in batch or continuous mode. A batch pyrolysis system is usually implemented for smaller capacities. The process cycle consists of several stages: (a) raw material loading, (b) system pre-heating, (c) pyrolysis, (d) temperature reset (cooling) and (e) end-products collection. A batch process requires quite extensive manual labor.

In spite of the relatively low initial investment needed, batch units have proved to be less economically viable compared to continuous. Across the world, Asia remains the geographic region where the majority of pyrolysis-based tyre recycling units is located; however, these are mostly low capacity plants targeted to energy valorization of ELTs. Several laboratory and bench scale (conventional or more innovative) ELTs pyrolysis reactors are documented, while there are only few pilot/demonstration or industrial applications. Pilot units operated so far are mainly based on batch rotary kiln reactors, aimed at producing both energy and carbonaceous materials. The key influence on the product yields, gas and oil composition, is the type of reactor used, which in turn determines the temperature and heating rate applied. The experience gained from experimental and pilot ELTs pyrolysis systems proves that small scale batch reactors and continuous rotary kiln

reactors, can be upgraded up to commercial scale (Williams, 2013). Rotary kilns are used to heat solids to the point where the required chemical reaction(s) takes place. The rotary kiln is basically a rotating inclined cylinder. Solids retention time in the kiln is an important design parameter and is set by proper selection of the diameter, length, speed, slope and internal design. There are two basic types of rotary kilns; directly and indirectly fired.

At temperature above approximately 250°C , shredded tyres release higher amounts of liquid oil products and gases, while above 400°C , the yield of oil and solid tyre-derived char may decrease relatively to gas production. During pyrolysis at high temperatures, vulcanized rubbers are quickly decomposed to low molecular weight olefins (MW 300–400). High molecular weight compounds can be generated in low pyrolysis temperatures and longer residence times. New technological breakthroughs are necessary for the commercialization of low temperature pyrolysis (Bianchi et al., 2014; Díez et al., 2005; Martínez et al., 2013a).

Experimental studies have proved that pyrolysis under vacuum resulted not only in lower energy requirements for the process, but also to a better control of the received products (Chaala and Roy, 1996; Lopez et al., 2009; Roy et al., 1995). Fast or catalytic pyrolysis can be used in order to increase the yield of valuable hydrocarbons (Aguado et al., 2005; Shah et al., 2009; Williams and Brindle, 2003). The substitution of N_2 or He with hydrogen, aids to the minimization of coking and repolymerisation reaction, resulting also to lower operational temperatures ($350^{\circ}\text{C} < T < 400^{\circ}\text{C}$), maximization of liquid product yield and high quality products (Mastral et al., 2000). However, the aforementioned types are more sophisticated and include a higher operational cost.

ELTs pyrolysis in a rotary kiln operated at 550°C on the other hand, is preferred for a char oriented process, while at the same time beneficial yield and characteristics for the produced oil are acquired. In Fig. 3 the experimental results from an operating rotary kiln are depicted. The experiments performed, aimed to determine the best operating parameters. More specifically, three available groups of ELTs were pyrolysed, regarding their particle size which ranged between (a) 5–10 mm, (b) 10–15 mm and (c) 15–20 mm. Additionally, four final pyrolysis temperatures were tested ($450\text{--}500\text{--}550\text{--}600^{\circ}\text{C}$) under two heating rates $20^{\circ}\text{C}/\text{min}$ and $60^{\circ}\text{C}/\text{min}$. At 550°C maximum char yield is achieved, for both heating rates applied. Additionally, the produced pyrolytic oils in the rotary oven, were more aromatic and had lower oxygen contents, due to their higher residence time in the hot zone of the reactor (Acevedo and Barriocanal, 2014; Acevedo et al., 2013).

3.3. SGP III: activate char

Numerous laboratory-scale experimental results prove that activation of an ELTs-based char, results to activated carbon with medium adsorption capacity (Al-Saadi et al., 2013; Aranda et al., 2012; Gupta et al., 2013, 2011; Mui et al., 2004). More specifically, there are two main steps for the preparation and manufacture of activated carbon: Carbonization of the carbonaceous raw material up to 800°C , in the absence of oxygen, and activation of the carbonized product (carbon black). During activation, the carbon content is consumed towards pore deepening and pore development, under the presence of chemical substances; based on international literature, activation can be either physical or chemical. However, this categorisation lacks of accuracy, since during “physical” activation, either by CO_2 or steam, at carefully controlled conditions (high temperatures) chemical reactions are involved, (i.e. $\text{C} + \text{CO}_2 = 2\text{CO}$ or $\text{C} + \text{H}_2\text{O} = \text{CO} + \text{H}_2$).

“Physical” activation is a two-step process. After carbonization the resulting char is activated at elevated temperatures with oxidizing agents including, either carbon dioxide, steam, air or their mixtures. As an activating agent, CO_2 is clean and easy to handle.

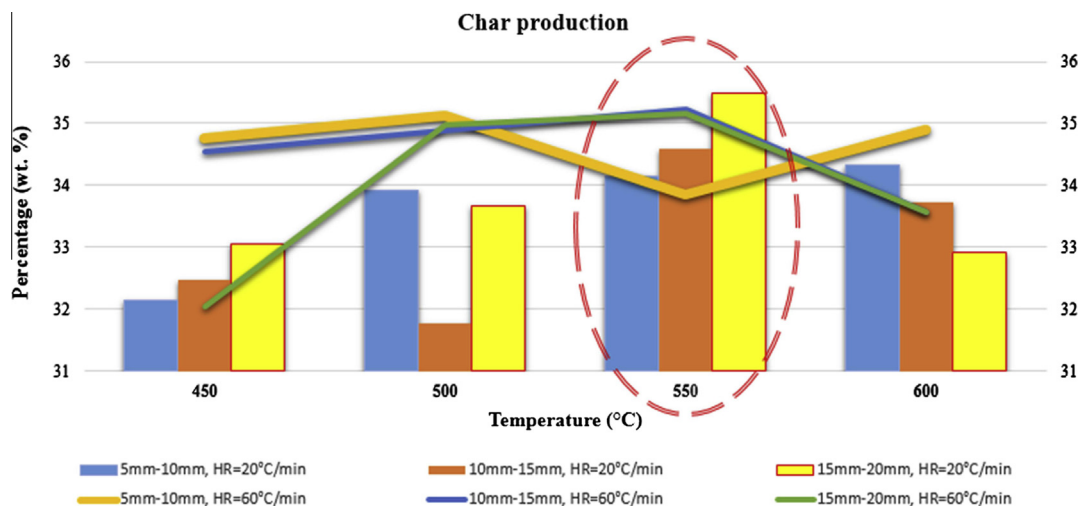


Fig. 3. Selection of optimum conditions for ELTs pyrolysis.

Due to the slow reaction rate it facilitates control of the activation process, at temperatures around 800 °C. Steam on the contrary, is preferred than CO₂ because it causes faster diffusion in the porous matrix under a faster reaction rate (Marsh and Reinoso, 2006; Mui et al., 2004). During “chemical” activation, the two steps are carried out simultaneously, with the precursor being mixed with chemical activating agents, as dehydrating agents and oxidants. Chemical activation is carried out in a single step, performed at lower temperatures and therefore resulting in the development of a better porous structure (Ioannidou and Zabaniotou, 2007).

The comparison of several activation processes, highlight that physical activation with steam at temperatures between 800 °C and 1000 °C under high residence times, are considered the most suitable operating conditions (Mui et al., 2004; Zabaniotou et al., 2004). In the case of a batch pyrolysis process, one stage pyrolysis/activation rotary kiln is proposed. On the contrary, for the case of a continuous pyrolysis process, a dual hybrid system is suggested.

3.4. SGP IV: produce marketable products

Pyrolysis products are distinguished in three different categories, with a variety of possible applications for each case. Pyrolytic gas can be used, if cleaned, as a gas fuel due to its high LHV (>20 MJ/Nm³), sole, or mixed with natural gas/propane in a pre-determined ratio, in simple appliances, providing energy/heat where needed. This could be proved a very interesting route for pyrolytic gas utilization, saving at the same time an appreciable quantity of natural gas, provided that certain modifications of low scale would be completed (Honus et al., 2014).

Environmental concerns are related to Sulphur, Zn and Chlorine. Although, sulphur is identified in the gas, in the form of H₂S, this is of maximum concentration <750 mg/Nm³ (Berruoco et al., 2005; Edwin Raj et al., 2013; Hu et al., 2014). Regarding the emissions produced from the combustion of pyrolysis gas, these should be below the limits established by the Waste Incineration Directive; this is valid for CO_x and NO_x emissions but not for SO₂ emissions (4300 mg/Nm³ are emitted compared to the maximum allowed of 50 mg/Nm³) (Aylón et al., 2007). Due to the applied operational conditions, Zn and chlorine formulations are not expected to occur; Zn boiling point is well below pyrolysis operational temperature and chlorine is almost retained to the solid fraction (Dřez et al., 2004; Martínez et al., 2013b). Any problem associated with the above, can be tackled by using a proper burner, or an acid gas

cleaning system to reduce the HCl and SO₂ concentration (Aylón et al., 2007).

Pyrolysis oil density, viscosity, calorific value and flash point were found comparable to those of the commercial automotive diesel fuels (Cunliffe and Williams, 1998; Frigo et al., 2014). ELTs pyrolysis oil includes aromatics, non-aromatics, oxygenated aromatics, oxygenated non-aromatics and nitrogenated aromatics or nitrosulphurated aromatics (Chaala and Roy, 1996; Choi et al., 2014; de Marco Rodriguez et al., 2001). Sulphur content on the liquid product represents 25 wt.% of the initial sulphur and is calculated not to exceed 1.2 wt.% (Berruoco et al., 2005; Edwin Raj et al., 2013). The sulfur content of the pyrolytic liquid is significantly higher (0.85–0.96 wt.%) than today's ULS Diesel (<15 ppm), but comparable to marine DMB and DMC distillates (typ. 2 wt.%) (E.P.A., 1999). Therefore, it can potentially be used to displace some marine fuel, especially in sea areas outside SECAs where fuels with an upper sulphur content of 3.50 wt.% until 1 January 2020 can be used (E.U.-Directive, 2012), thus acquiring financial benefits; the price of marine heavy fuel oil (HFO) exceeds \$800/metric ton (Bunkerworld, 2014).

Beyond the aforementioned, ash content and impurities concentration should be also minimized. Alternatively, the produced oil can be further upgraded by desulfurization and distillation process, either post or ante and optionally, with the use of catalyst (Chen et al., 2010; Laresgoiti et al., 2004), finally resulting to a fuel which can be included in the wider variety of alternative fuels of the upcoming years, (Martínez et al., 2014). Apart from modifications on process parameters and reactor characteristics, pyrolysis of pre-devulcanised tyre particles, was proved to assist to elevated yields for pyrolytic oils under the same conditions, as compared to conventional ones (Kebritchi et al., 2013).

Char from pyrolysis contains the non-converted carbon and can be used as a filler, an adsorbent and/or as an additive in composite materials production. Pyrolytic char or pyro black can be used as carbon black in tyres manufacturing industry or if further valorised via activation process, towards the production of carbonaceous adsorbents. The last, can ultimately lead to the production of a high added value, fully marketable material, with significant adsorptive properties, finding innumerable applications in gas and liquid stream purification processes. Research nowadays aims to valorise pyrolysis char for the production of catalytic materials.

The pyrolytic char produced by slow rotary kiln pyrolysis of a pretreated tyre is of low capability (60 m²/g < S_{BET} < 82 m²/g), but almost similar to the commercial carbon blacks (N-351, N-650) (Mastral et al., 2000). The produced char is not carbon black, but

a carbon char or pyro-char of lower quality (structure and size) and of increased ash content compared to virgin carbon black (de Marco Rodriguez et al., 2001). Ash content on ELTs char varies as a result of tyres manufacturing process and operation conditions applied; additionally sulphur and chlorine are also detected. For the case of sulphur, 70% of the initial amount is retained to the solid whereas the majority of chlorine is also retained to the solid state (Berrueto et al., 2005; Díez et al., 2004; Hu et al., 2014; Martínez et al., 2013b).

Regarding heavy metals presence in the solid product, Zn compounds were identified by XRD analysis and SEM micro analysis. ZnO was identified at temperatures below 700 °C. At higher temperatures (<1000 °C) zinc sulphide is formed, in the crystalline form of sphalerite (López et al., 2013). At temperatures exceeding 1000 °C, Zn is vapourised to the gas phase (Williams, 2013). However, due to its stability and its overall low percentage in the sample, its implication on fluid adsorption processes should be considered as minor. Consequently, the above affect the end product's selling price, which should be competitive to carbon black.

Based on the aforementioned, through ELTs-char activation, either by steam or CO₂, activated carbons with satisfactory structural and surface characteristics will occur. The produced ELTs-based activated carbons were found efficient for: mercury adsorption (flue gas decontamination) (Skodras et al., 2007), mercury chloride (HgCl₂) removal (a major mercury derivate emitted from municipal solid waste incinerators) (Ie et al., 2012), PCDD/F removal (incinerator flue gas) (Hajizadeh et al., 2011), NO₂ removal from waste to energy plants (Hofman and Pietrzak, 2011) and gaseous polycyclic aromatic hydrocarbons (PAH) abatement (Aranda et al., 2012). Applications of activated carbons from ELTs are also reported in natural gas storage and air pollution control (Brady et al., 1996). They can also be used for liquid-phased environmental depollution applications (Chan et al., 2012; Mui et al., 2010) including, cationic dye removal (Li et al., 2010a; Tanthapanichakoon et al., 2005), heavy metal removal from water (Gupta et al., 2012; Skodras et al., 2007), cadmium (II) ion removal from aqueous solutions (Al-Saadi et al., 2013), Ni(II) ions removal (Gupta et al., 2014) and lead adsorption (Saleh et al., 2013). Liquid phase entrapment of organic substances (Troca-Torrado et al., 2011) as well as pesticides removal (Foo and Hameed, 2010; Gupta et al., 2011; Ioannidou, 2011) were also documented.

Although, products from ELTs pyrolysis have traditionally been of relatively low quality with limited market penetration, refining these products into high value added materials to meet market specifications requires capital investment and operating expenses that have tended to make ELTs pyrolysis cost-prohibitive from a competitive standpoint. The recovery of additional secondary products, including besides rubber materials, steel and fibre represent between 15% and 25% of the untreated ELTs (Antoniu and Zabaniotou, 2013). While markets for the rubber portions of the waste tyre are varied, markets for the steel and fibres are more limited, but emerging. Steel is recovered through the pretreatment process and can be sold with the condition that it does not contain rubber. During cryogenic processing, the obtained steel is cleaner and therefore has a higher value. The separated steel, if compacted, has a higher value to the scrap steel processor. A proven market for the separated steel corresponds to niche steel manufacturers using small, sophisticated electric arc furnaces, in civil engineering applications (where it is possible to re-utilize the steel fibre and the rubber of the waste tyres) (Centonze et al., 2012), or in concrete reinforcement (Graeff et al., 2012; Papakonstantinou and Tobolski, 2006). The separated fibres represent a mixture of nylon, rayon and polyester, slightly contaminated by rubber materials and minute shards of steel. The identification of markets or proposed uses for the exported fibres, remains unaddressed (California Integrated Waste Management, 2003).

3.5. SGP V: optimize energy efficiency

It has to be noticed that the production of a carbonaceous material with upgraded characteristics equivalent to commercial adsorptive materials suggested here requires the contribution of two energy-intensive processes, pyrolysis and activation. However, the high energetic content of the raw material and the adaptation of several heat/energy conservation techniques, of industrial origin, can efficiently reduce the energy needs.

Aiming to optimize energy efficiency, through this study, the activated carbon production process is suggested to be part of the integrated tyre pyrolysis-activation production complex. Through this practice, pyrolysis by-products (gas and oil) will be directly consumed to supply with the necessary heat/energy required for the process. It was reported that a large scale pyrolysis operation requires 0.2 KW/kg of processed sample (Li et al., 2010b).

Literature findings on hard coal-derived activated carbons production reported by other researchers, show a high diversification regarding the energy required for the dual process under physical activation; 22.14 KW/kg of produced activated carbon (Gabarrell et al., 2012) and 9.12 KW/kg of produced activated carbon (Bayer et al., 2005), whereas 3.13 KW/kg of produced activated carbon were reported for the chemical activation of olive waste cake (Hjaila et al., 2013). Studies concerning activated carbon production by ELTs as raw material are lacking behind (no study reported in the international literature).

Aiming to provide ELTs data for comparison with the above, Table 1 presents the results of the two-stage process performed in this study (pyrolysis and activation). It was calculated, that by the recycled-use in plant of pyrolysis gas, 6.36 KW/kg of produced activated carbon can be produced (without gas cleaning needed), resulting in an energy gain by reducing the energy needs of the process. A surplus energy can be extracted if pyrolytic oil could be combusted; however this requires an additional treatment cost. Unless the treatment cost is reduced, the pyrolytic oil might be directed to refineries or used as a marine fuel or No. 2 fuel oil, or as heating oil; its selling price could secure financial benefits, thus strengthening plant's viability. In parallel, due to the high operational temperature, heat recovery can also be achieved in various sections of the process, thus limiting the overall energy demand to low levels. Additionally, the installation of co-generation units as well as of a boiler economizer responsible for steam (as activation agent) production, are also proposed.

4. Barriers to implementation

4.1. Barrier I: misleading legislation

EU is committed to achieve ambitious goals for sustainable environmental management, not only by reducing greenhouse gas emissions but also to ensure that wastes are treated in a way that minimizes environmental impacts. The vast annual production of ELTs represents a huge loss of valuable resources that have

Table 1
ELTs pyrolysis and the consequent activated carbon production process characteristics.

Mass balance		Operational conditions	
<i>ELTs pyrolysis</i>			
Char yield (wt.%)	35.5	Temperature (°C)	550
Liquid yield (wt.%)	43.0	Heating rate (°C/min)	20
Gas Yields (wt.%)	21.5	Residence time (min)	10
<i>Adsorptive materials production (1 kg)</i>			
Burn-off	62.5%	Required ELTs	7.51 kg
Pyrolysis oil density (kg/dm ³)	0.963	Produced Pyrolysis oil	3.89 dm ³
Gas LHV (MJ/Nm ³)	20.5	Pyrolysis gas	22.92 MJ

the potentials to be used as a fuel, or a precursor material for marketable end-products. European Union anticipates an increased interest of projects and investments that valorize ELTs towards Materials and Energy; for this reason, a series of regulations for Waste Tyre Management were set, including the European Commission's Landfill Directive (1999/31/EC), which banned the landfill of certain whole and shredded tyres effective from July 2003 to July 2006, respectively (E.U.-Directive, 1999) and the European End of Life Directive (2000/53/EC) which sets a target of 95% recovery by 2015 (E.U.-Directive, 2012). The main objective of Directive (2000/53/EC) is the prevention of waste from vehicles, in addition to, the reuse, recycling and recovery of end of life vehicle components, so as to reduce the disposal of wastes.

Although these two directives have had and continue to have an impact on ELTs management, with the development of strategic programs, such as the producer responsibility initiative set up by the European Tyre Manufacturers in 14 countries (ETRMA, 2010), the over reliance on rubber derived products still continues to have a significant effect on the environment. According to European Directive 2008/98/EC on waste (Waste Framework Directive), tyres can reach end-of-waste status, as long as they fulfill end-of-waste criteria (WFD, 2008). These legislation acts aid substantially to environmental protection, through the gained environmental and economic benefits. As a result, product manufacturing using less virgin raw materials is achieved; in parallel, less wastes are to be eliminated. To facilitate and promote the use of ELTs pyrolysis for recycling, additional end of life criteria need to be established for the pyrolysis products, in order to ensure high levels of environmental protection, while enhancing the economic feasibility of the process from the production of valuable materials.

Legislation can affect both the cost and the long term viability of pyrolysis process in addition to the environmental and economic costs associated with the overall management of tyre waste. Therefore legislation should: (i) ensure that ELTs can only be disposed of through authorized/certified disposal routes, (ii) govern the operation of ELTs transporters, sorters storage facilities and processing facilities and (iii) recognize ELTs derived products as alternative energy sources or secondary raw materials with respect to criteria identified and certified through regulations (ETRMA, 2010). The introduction of standards for ELTs derived products is a key for their recognition as an alternative energy source or secondary raw materials. Ultimately legislation will impact economic and environmental costs. The proper enforcement procedures must also be put in place to make sure that the legislation is respected.

In Europe, each Member State has the obligation to be in compliance with the EU legislation in transposing the directives into local (national) legislation. Each Member State is free to choose and set the initiatives and the manner through which, it will be able to reach the European posed targets. In order to achieve this goal, three different schemes have been established, and each country has to choose the most suitable among them (ETRMA, 2010).

As discussed in the previous paragraphs, the potential advantages of slow pyrolysis process, include not only the possibility of recovering the organic fraction's material value plus an increased electrical generation, but also in a lesser extent, the recovery of several useful constituents, from which the raw material may consist of; thus sustaining valuable resources. However, despite the detailed description of the process and the advantages originated from the valorisation of the expected products, the current EU legislation includes, but not distinguishes, pyrolysis process in the more conventional incineration regime; thus not promoting its implementation, despite its proven, low environmental impact (Antoniou and Zabaniotou, 2013).

A bottleneck in legislation inhibits industrial application of pyrolysis, especially in countries which have developed national legislation in perfect accordance with EU. This bottleneck relates strongly to the incapability of the legal term that defines depolymerisation of tyres, while not separates gasification or pyrolysis from incineration. Moreover, combustion processes when implicate the use of ELTs as a fuel (main or substitute), generate gaseous pollutants and solid waste materials which must be disposed of or re-used as secondary raw materials. Tyre combustion in comparison with conventional fuels is responsible for a significant increase in atmospheric zinc emissions and for elevated zinc levels on the solid product, while the opposite trend was noticed for nitrogen oxides into the atmosphere (Gieré and Stille, 2004).

On the contrary, pyrolysis is an energy and material recovery process and should differentiate from incineration. The categorization of depolymerisation (Pyrolysis) as incineration in the Waste Framework Directive has an effect on the Planning, Design and Construction of the pyrolysis plant and to social acceptance as well (Samolada and Zabaniotou, 2012). Efforts should be taken in order to modify EU Legislation towards differentiation of pyrolysis from incineration.

4.2. Barrier II: shortage of environmental standards

Pyrolysis products have historically yielded poor returns due to their low selling prices; as a result, the majority of pyrolysis plants have not proved commercially successful (Antoniou and Zabaniotou, 2013). Pyrolysis plants are mostly located in Asia due to the less strict limits in environmental standards. Existing environmental restrictions on wastes incineration can be potentially sufficient for ELTs pyrolysis exhausts. More specifically, the lower pyrolysis operating temperatures compared to the combustion – incineration, results in a less pollutant gas effluent, but also to an increased concentration of both Cl and S in the obtained char (Diez et al., 2004). Combustion with the presence of chlorine, heat and oxygen, results in dioxins' production, while during pyrolysis under inert atmosphere, dioxins are not produced (Aguado et al., 2005; Fink, 1999).

Establishing of waste criteria is crucial as they define the technical criteria for determining when a waste ceases to be a waste without endangering any aspects of human health and environment. According to the Waste Framework Directive a certain waste may only cease to be a waste if: (i) the substance or object is commonly used for specific purposes, (ii) a market or demand exists for such a substance or object, (iii) the substance or object fulfils the technical requirements for the specific purposes and meets the existing legislation and standards applicable to products and (iv) the use of the substance or object will not lead to overall adverse environmental or human health impacts (E.U.-Directive, 2008).

4.3. Barrier III: shortage of BAT (Best Available Techniques)

The adopted by the European Commission BREF document (8/2006) on the Best Available Techniques for the "Incineration of Wastes", contains few aspects on the pyrolysis of MSWs and even fewer on ELTs pyrolysis (EU-BREF, 2006). BREF, an European BAT reference document, along with the EU Directive 2000/76/EC states that pyrolysis process may be directed to the thermal treatment of some municipal wastes, sewage sludge, synthetic wastes, used tyres, cable tails and metal and/or plastic compound materials (WID, 2008).

Since pyrolysis is a well-studied operation in international literature, the non-establishment of a list of Best Available Techniques stalls its implementation for a variety of raw materials, including biomass, ELTs and MSWs.

4.4. Barrier IV: lack of standardization

The financial profitability of ELTs pyrolysis plant should be secured to attract the interest of investors/entrepreneurs. Tyre-derived products should fully conform to technical standards and specifications in order to be competitive to other marketable products with analogous characteristics. Specifications for the materials originated from ELTs should include every aspect regarding their production, assessment and utilization, in order to reduce the obstacles to inter-regional and international trade. Currently the European Tyre Recycling Association is working to improve the standards for the ELTs based products.

Towards this scope, ETRA contributed to the development of CEN/TS 14243:2010, a standardization test concerning materials produced from ELTs (Specification of categories based on their dimension(s) and impurities and methods for determining their dimension(s) and impurities), which provides definitions for the categories of materials originated from ELTs (ETRA, 1996; ETRMA, 1959; UNI-CEN/TS-14243, 2010). It also provides test methods for the determination of the dimension(s) of the materials produced from all categories of ELTs at all steps of the treatment process as well as for the determination of impurities (UNI-CEN/TS-14243, 2010).

Alongside, PAS 107, prepared by the British Standards Institution (BSI) in collaboration with WRAP (Waste and Resources Action Programme), aims also to provide a detailed spectrum of specifications for waste materials (PAS-107, 2012). PAS 107 defines minimum requirements for the initial storage, production and final storage of size reduced, tyre derived rubber materials, while excluding the use of whole or baled tyres in end use applications.

For a broader implementation of ELTs pyrolysis, scale up and pilot demonstrations are needed along with dissemination of results and public awareness. Demonstration projects are necessary in order to unlock technical difficulties as well as to increase material and energy efficiencies. Following, product manufacturing should encompass certain validation and standardization methodologies. Product standardization not only stems from, but also even influences economic and societal aspects, creating confidence, securing public health and ensuring the smooth flow of local and international trade, while reducing environmental and financial risks.

4.5. Barrier V: safety and health

REACH (Registration, Evaluation, Authorisation and Restriction of Chemical substances) regulation aims to improve “the protection of human health and the environment, through the better and earlier identification of the intrinsic properties of chemical substances, while enhancing innovation and competitiveness of the EU chemicals industry”.

Up to present, REACH took under consideration only the data from tyre manufacturing companies. However, ELTs pyrolysis, an innovative alternative, is possibly responsible for the production of questionable substances. Pilot pyrolysis plants should be promoted in order to fully investigate the pyrolysis process and its expected products, completing up to a certain extent the REACH regulation, thus setting pyrolysis as an equivalent competitor, regarding thermochemical valorization, to incineration.

Published scientific articles studying the overall effects of ELTs pyrolysis to date are scarce but some published work found that grinding stage is responsible for GHG emissions. More than mechanical grinding, cryogenic crushing is responsible for greenhouse effects and increased water and energy consumption (Corti and Lombardi, 2004).

Results from a comparative analysis of several methods of ELTs management under LCA criteria, assessed pyrolysis as the method

with the lowest environmental impacts compared to ambient grinding, devulcanization and illegal tire oil extraction. More specifically, ELTs pyrolysis impact on respiratory (organic and inorganic) and carcinogenic effects stems only from pyrolysis gas use and marks values well below the other methods. Regarding process's effect on ecotoxicity, acidification/nitrification and fossil fuels, pyrolysis is the process with the lowest environmental impact, thus responsible for less environmental hazards (Li et al., 2010b).

For the integrated ELTs pyrolysis system successful implementation in the future, a close collaboration between the Member States, ECHA (European Chemical Agency), tyre manufacturers and ELTs operators is proposed, contributing in a maximum degree to the categorization of substances to potentially carcinogenic, mutagenic or toxic to reproduction (CMR category 1 or 2), persistent, bioaccumulative and toxic (PBT) or very persistent and very bioaccumulative (vPvB), (REACH, 2006).

4.6. Barrier VI: lack of sustainability and LCA assessment

In order to assess an integrated ELTs valorization plant towards high added value materials production as also proposed by this study, sustainability backup regarding environmental, health and safety matters and social acceptance should be also studied. A tool that combines several parameters regarding environmental impact assessment supplying also with valuable inputs to identify appropriate solutions for managing solid waste is Life Cycle Assessment (LCA); however only few LCAs have been developed to study ELTs valorization (Clauzade et al., 2010; Corti and Lombardi, 2004; Li et al., 2010b).

An LCA could also highlight the crucial aspects of a complete operation either targeted to solid materials or electricity production.

4.7. Barrier VII: associated costs and economic viability

The costs affecting the development of a viable depolymerisation process include: pretreatment costs, equipment and infrastructure cost, process development cost, operating costs, energy costs, product post-treatment cost, product certification costs, product storage, marketing, security of location, product price, production capacity, total production cost, capital investment and the applied tipping fee (Stavropoulos and Zabaniotou, 2009).

Another parameter able to influence the decision-making process is the ELTs collection method. A non-collected and dispersed system may characterize an investment in smaller-scale facilities, as prohibitive. On the other hand, large capacity production units will be required to provide attractive economics; this would possibly pose problems in small markets.

Products characteristics and yields affect also economics; the selling price of the produced carbonaceous material, primarily depends on its qualitative characteristics (adsorption capacity, ash content, pore volume distribution) and secondly on product yield (Stavropoulos, 2005; Stavropoulos and Zabaniotou, 2009).

The effectiveness of wastes to material and energy valorization systems has already been critically debated in light of the changing needs of society. However, as economic stability in each EU Member State remains questionable, easily adjustable solutions should be applied. Typical example of a successful attempt to remove these barriers is the adoption of the tipping fee during ELTs collection. The gate fee can cover the transportation cost of the ELTs to the facility as well as the variable costs of processing. To date, there are variations on tipping fees recorded, mostly based on the size of the collected sample (the bigger the dimension the higher the tipping fee), (Samolada and Zabaniotou, 2012). The payment of the

fixed costs of the business and the generation of profit are then derived purely through sales of the end product.

Today's challenge is to specifically choose the desired properties of the end products, by the careful selection of operating parameters. However, due to the nature of the received products purification processes are essential, lowering significantly, in some cases, the financial profit. More specifically, these processes are directed to minimize sulphur content (in the form of H_2S) in ELTs pyrolysis gaseous and liquid products (Hu et al., 2014). By ensuring the marketability of pyrolysis oil, or alternatively, promoting an internal use for plant's energy needs, encouraging economic indices are expected to occur (Chen, 2014). The successful commercialization of the produced char, as a solid fuel or as an adsorptive material should be also subjected to strict environmental regulations. An improvement of economic indicators of the plant, can occur from the surface modification of the solid product, according to the proposed end-use (heavy metal adsorption, organic pollutants, mercury, liquid phase adsorption applications).

Finally, the decision for a tyre depolymerisation plant for a waste management company, will depend on whether the pyrolysis operating costs are less than that of combustion (Samolada and Zabaniotou, 2012). More specifically, the size of the plant is a parameter of great importance for pyrolysis economics. Medium commercial scale plants are economically feasible, compared to small commercial ones (Islam et al., 2011). Particle size can also significantly affect the cost of an operating ELTs pyrolysis process, since there is a direct connection of the necessary time for the completion of the thermal decomposition with ELTs particle size (Haydary et al., 2012).

A ELTs pyrolysis plant should be targeted to the production of solid adsorptive materials; this way the financial sustainability of the plant could be strengthened by the selling of pyrolytic oil and extracted steel.

Labor cost, of course, is a critical parameter. A case study performed is based on geographical regions with low labour costs inside EU (Eurostat, 2014; Peters et al., 1968). Parameters of the feasibility study performed under the project (Stavropoulos and Zabaniotou, 2009) are provided in Table 2. In low labor countries tax in products and services is around 20%. The selling price of the end product is similar to markets prices: a common selling price (bulk) for an adsorbent directed to dye/pesticides removal is 2\$/kg. Additionally, the selling prices of crude pyrolysis oil and exported steel cords are determined to reach 400\$/tonne and 75\$/tonne, respectively (Islam et al., 2011). Crude pyrolysis oil is suggested to be directed to market as a heating fuel rather than marine fuel as proposed above, due to the lack of standardization and of non-acquired permissions. On the contrary, since the pyro-gas selling price is low, it is proposed to be recycled and used either to maintain the high operating pyrolysis temperatures or as a gas

fuel for the consequent, activation process. The extracted results, regarding plant's economic indicators, as well as the necessary assumptions made, are presented in the following Table 3.

The results from the study indicate that such a facility could be economically viable (POT = 1.77 years) in countries of low labor. Aiming towards an economically viable pyrolysis plant, raw material supply chain and the subsequent introduction of the end-products to a designated market should be taken under consideration.

Emerging pathways towards production of valuable chemicals from pyrolytic oil can also a strategy; however, purification process's cost and low yields, set limits to this valorization route.

4.8. Barrier VIII: difficult penetration in conservative markets

The market for waste tyres treatment is a long-term growing market. Financial and legislative tools can play a significant role in ELTs management (Chang, 2008). The product characteristics from an industrial-scaled pyrolysis plant, operating under sustainable and eco-friendly principles, which reuses or diminishes any harmful by-products, constitutes the milestone for market penetration. Plant capacity should be calculated at the break-even point and according to the proposed market. Large capacity production units will be required to give attractive economics and this may pose problems in small markets (Stavropoulos and Zabaniotou, 2009).

The report "End of life tyres", published in 2010, European Tyre & Rubber Manufacturers Association (ETRMA) states that "Under current market conditions the economic viability of these options has yet to be proved (there are few or no large-scale plants currently in operation) but they have the merit to offer scope for increasing recycling rates" (ETRMA, 2010).

For pyrolysis market penetration, the proposed design and operating conditions should be primarily approved by the regulatory authority, provided that the systems are designed and operated in a way that the energy efficiency and Emission Limit Values (ELVs) can be achieved. Additional technical information may also be requested to the regulatory authority, to justify alternative design and operational parameters. Once approved, these parameters are reflected in the operational permit(s) and/or conditions set out for the facility (EPD, 2011).

4.9. Barrier IX: raw material availability and supply

Availability and supply of resources can be affected by the collection system and the management system applied. A limited supply of raw materials can prevent the establishment of a pyrolysis plant, in certain geographic areas. Not all European countries apply the same management systems. Apart from the previously described Producer Responsibility system, Tax System and Free Market System are also available. Due to various developed methods for tyres valorization, this lack of resources was noticed and discussed during the 2012 ETRA Annual Conference (ETRA, 1996, 2012).

Raw material availability along with raw material cost (low cost or even better free of charge are preferred) and plant capacity are cost affecting factors of an ELTs pyrolysis plant.

4.10. Barrier X: public's great skepticism

In parallel to technological development, the initial step in launching ELTs pyrolysis applications to a bigger scale is to develop awareness and matters of sustainability within the local community. By the time the perception, that ELTs valorization, through pyrolysis, for energy and materials is strongly connected to zero waste principles, then pyrolysis implementation will be eased. This awareness will be strengthened with demonstration programs that

Table 2
Parameters used in cost estimation.

Plant capacity	30 tonnes/day of ELTs
Location, time, currency	EU 2014, US\$
Annual operating time	7920 h @ 24 h/day
Maintenance	6% of FCI
Feedstock cost	0 US\$/tonne
Labor rate	3.70 US\$/h (regular duty/8 h/day)
Total labors (in equivalent of shift operators)	5
Electricity needs	Supplied by pyrolysis gas
Interest rate	7%
Plant life	10 years
Activating carbon selling price	2\$/kg
Pyrolysis oil selling price	0.4\$/kg
Steel cords selling price	0.075\$/kg

Table 3

Assumptions and calculated economic indicators regarding marketable adsorptive materials production from ELTs hybrid process.

Capacity (tonnes/day)	Operation (days/year)	Product yields (wt.%)				Activated carbon yield (wt.%)	Price (\$/tonne)			
		Char	Oil	Gas	Ash		ELTs	Activated Carbon	Pyrolysis oil	Steel
<i>Assumptions</i>										
30	330	0.3	0.5	0.15	0.05	0.133	0	2.00	0.4	0.075
Total capital investment		Total fixed operating costs		Variable operating costs		Contingency		Total operating costs		
<i>Economic indicators</i>		1.829.765		756.000		77.573		2.663.338		
Total production cost		Annual sales revenue		ROI		NPV				
				Before tax		Post tax		Before tax		Post tax
3.179.411		4.724.775		0222		0086		26.227.342		19.590.374

can attract citizens' attention. The encouragement of the public's active participation in every step of the unit's authorisation procedure, as well as during its operation, will result in an increased acceptance of the process. The latter was promoted also by the EU policy, 25.10.2011COM (2011) 681 final (Samolada and Zabaniotou, 2012).

It is believed that the revision of the legislation on the proper definition of pyrolysis as a recovery method and not as incineration, will foster its social acceptance.

5. Drivers

The most important drivers of pyrolysis are related to transforming waste material into marketable products and recycling rubber in an energy-efficient process, while aiding to lessen greenhouse gas emissions but also, to conserve natural resources that would otherwise be wasted.

5.1. Driver I: ensuring sustainable use and efficiency of resources

Towards a more effective, eco-efficient ELTs management, matters including environmental protection, resources maintenance and energy demand, require an integrated approach (Antoniou and Zabaniotou, 2013). In cases where reuse and recycling proved inefficient, large quantities of scrap tyres ended up in landfills each year. The landfilling of scrap tyres is responsible for several problems, due mostly to their tendency to rise to the surface, harming landfill covers (RMA, 2009). However in Europe, landfilling of ELTs is prohibited from 2003 and 2006 for whole tyres and shredded tyres, respectively (E.U.-Directive, 1999). In order to avoid the above mentioned environmental consequences and to provide sustainable and environmental friendly solutions in ELTs management with simultaneous high added value material production and energy recovery, pyrolysis can be used as an innovative alternative solution.

Pyrolysis is in accordance with the European Union's Waste Framework Directive of 1975 (Directive 75/442/EEC); this directive introduced for the first time the waste hierarchy concept into European waste policy. In 2008, the EU parliament introduced a new five-step waste hierarchy to its waste legislation Directive 2008/98/EC; this directive, should be introduced in each Member State's waste management laws (WFD, 2008). Furthermore, the importance of waste minimization, the protection of the environment and human health were outlined in a following directive. Pyrolysis was characterised as an attractive thermochemical process to tackle with ELTs disposal problem, resulting also to energy recovery.

5.2. Driver II: towards near-zero waste at European and global level

By implementing pyrolysis in ELTs management, in parallel with investigation for niche markets for pyrolysis products, a zero waste method is achieved, encouraging a diversified ELTs valorisation option, apart from landfill, incineration and rubber granulate and rubber powder production. From an environmental perspective, the elimination of wastes represents the ultimate solution to pollution problems that threaten ecosystems at global, national and local levels. In addition, a complete valorisation of raw materials, accompanied by a shift towards renewable sources, contributes effectively to resources conservation (Curran and Williams, 2012).

5.3. Driver III: ELTs as a resource to recycle and recover materials

ELTs constitute a high calorific waste and thus they can be used as feedstock to pyrolysis conversion plants for both energy and carbon materials production. Alongside, a wide range of materials such as steel, fibers, shredders, oils and carbon fillers could be also recovered, since they represent key components of tyre manufacturing.

5.4. Driver IV: resource efficiency: growth markets for the future

Regarding European ELTs management, energy recovery is mostly achieved through co-combustion with coal in cement industries (93% in volume); however, this corresponds to a great loss of energy, taking under consideration tyres manufacturing process. Pyrolysis in comparison with incineration has the advantage of utilization of the solid residue; ELTs char can be further treated and become a valuable product. More specifically, through activation process, char's characteristics can be upgraded resulting to the formation of activated carbon. A highly mesoporous activated carbon obtained from ELTs char exhibits competitive characteristics to commercial adsorptive materials, characterizing it as eligible for: (a) liquid phase applications (dissolved organics, toxic and odour compounds removal), (b) air purification processes (volatile inorganics and organics removal) and (c) special applications, such as cigarette filters, cloth, gold mining and catalyst support (Marsh and Reinoso, 2006; Zabaniotou and Stavropoulos, 2003).

In addition, the process' liquid fraction, as a result of condensation of the produced gases, along with can be reintroduced into the process as a fuel, to supply with energy the thermal decomposition process. Alternatively, it can also be marketed as a sole product, depending on the amount of additional processing required. ELTs pyrolysis oil exhibits similar characteristics to No. 2 fuel oil, a low-grade petroleum product with some contamination (CEPA, 2006).

5.5. Driver V: promoting eco-innovative waste management as part of sustainable development

A wide range of related ideas are included in this frame including, from environmentally friendly technological advances, to socially acceptable innovative paths towards sustainability. An initiative to establish waste prevention programs, aiming primarily, to decouple economic growth from environmental impacts of waste generation and secondarily, to reduce the amount of wastes produced in each country, was completed in the end of 2013 (Wilts et al., 2013).

As a proof of eco-innovation, pyrolysis, is a promising, environmental friendly approach for ELTs effective valorization, thus establishing a new genre of innovative zero-waste processes for the waste management market. Apart from improving sustainability and environmental indicators for Europe, new job positions could be created. This could strengthen the image of ELTs utilization and recycling across European Union, thus creating profitable and competitive enterprises rather than obliging tyre producers/manufacturers.

6. Conclusions

Pyrolysis applications with competitive investment costs and significant incomes from products selling, provide evidence for business possibilities. Although, economical parameters affect the cost and implementation of ELTs pyrolysis including production capacity and cost, capital investment, product price and even tipping fee, and also the final destination of pyrolysis products can determine the overall economic balance. Especially, char valorisation towards high added value carbonaceous materials (activated carbon/catalyst support), can positively affect the economics of pyrolysis.

The overview of the legal and policy framework for pyrolysis highlighted the legislation bottlenecks. Significant improvement in ELTs pyrolysis market penetration can be achieved if some legislative barriers, such as differentiation of pyrolysis from incineration disappear.

Application of pyrolysis in industrial scale is also affected by supply of raw materials, lack of standardization and relatively low selling prices of the end products. In some cases, lack of public awareness coupled with low social acceptance has impeded progress.

Prior to a broader implementation, matters regarding identification of designated markets, investigation for replicability potentials of the endeavour and development of standards should be totally resolved in order to attract investors' interest.

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References

Acevedo, B., Barriocanal, C., 2014. Fuel-oils from co-pyrolysis of scrap tyres with coal and a bituminous waste. Influence of oven configuration. *Fuel* 125, 155–163.

Acevedo, B., Barriocanal, C., Alvarez, R., 2013. Pyrolysis of blends of coal and tyre wastes in a fixed bed reactor and a rotary oven. *Fuel* 113, 817–825.

Aguado, R., Olazar, M., Vélez, D., Arabiourrutia, M., Bilbao, J., 2005. Kinetics of scrap tyre pyrolysis under fast heating conditions. *J. Anal. Appl. Pyrol.* 73, 290–298.

Al-Saadi, A.A., Saleh, T.A., Gupta, V.K., 2013. Spectroscopic and computational evaluation of cadmium adsorption using activated carbon produced from rubber tires. *J. Mol. Liq.* 188, 136–142.

Antoniou, N., Zabaniotou, A., 2013. Features of an efficient and environmentally attractive used tyres pyrolysis with energy and material recovery. *Renew. Sust. Energy Rev.* 20, 539–558.

Antoniou, N., Samolada, M., Stavropoulos, G., Bruton, G., Zabaniotou, A., 2012. Challenges and Barriers for the End of Life Depolymerisation: The Depotec Project, PRE XI, Thessaloniki, Greece, pp. 1187–1196.

Aranda, A., Murillo, R., García, T., Mastral, A.M., 2012. Simulation and optimization of tyre-based steam activated carbons production for gas-phase polycyclic aromatic hydrocarbons abatement. *Chem. Eng. J.* 187, 123–132.

Aylón, E., Murillo, R., Fernández-Colino, A., Aranda, A., García, T., Callén, M.S., Mastral, A.M., 2007. Emissions from the combustion of gas-phase products at tyre pyrolysis. *J. Anal. Appl. Pyrol.* 79, 210–214.

Bayer, P., Heuer, E., Karl, U., Finkel, M., 2005. Economical and ecological comparison of granular activated carbon (GAC) adsorber refill strategies. *Water Res.* 39, 1719–1728.

Berrueto, C., Esperanza, E., Mastral, F.J., Ceamanos, J., García-Bacaicoa, P., 2005. Pyrolysis of waste tyres in an atmospheric static-bed batch reactor: analysis of the gases obtained. *J. Anal. Appl. Pyrol.* 74, 245–253.

Bianchi, M., Bortolani, G., Cavazzoni, M., De Pascale, A., Montanari, I., Nobili, M., Peretto, A., Tosi, C., Vecchi, R., 2014. Preliminary design and numerical analysis of a scrap tyres pyrolysis system. *Energy Proc.* 45, 111–120.

Brady, T.A., Rostam-Abadi, M., Rood, M.J., 1996. Applications for activated carbons from waste tires: natural gas storage and air pollution control. *Gas Sep. Purif.* 10, 97–102.

Bunkerworld, 2014. Bunker Index.

California Integrated Waste Management, B., 2003. Assessment of Markets for Fiber and Steel Produced from Recycling Waste Tires. California Integrated Waste Management Board, Sacramento.

Centonze, G., Leone, M., Aiello, M.A., 2012. Steel fibers from waste tires as reinforcement in concrete: a mechanical characterization. *Constr. Build. Mater.* 36, 46–57.

CEPA, 2006. Technology Evaluation and Economic Analysis of Waste Tire Pyrolysis, Gasification, and Liquefaction CalRecovery Inc, California.

Chaala, A., Roy, C., 1996. Production of coke from scrap tire vacuum pyrolysis oil. *Fuel Process. Technol.* 46, 227–239.

Chan, O.S., Cheung, W.H., McKay, G., 2012. Single and multicomponent acid dye adsorption equilibrium studies on tyre demineralised activated carbon. *Chem. Eng. J.* 191, 162–170.

Chang, N.B., 2008. Economic and policy instrument analyses in support of the scrap tyre recycling program in Taiwan. *J. Environ. Manage.* 86, 435–450.

Chen, K.W., 2014. The applicant feasibility study of recovered fuel after waste tire pyrolysis. *Adv. Mater. Res.* 852, 776–779.

Chen, T.-C., Shen, Y.-H., Lee, W.-J., Lin, C.-C., Wan, M.-W., 2010. The study of ultrasound-assisted oxidative desulfurization process applied to the utilization of pyrolysis oil from waste tires. *J. Clean. Product.* 18, 1850–1858.

Choi, G.-G., Jung, S.-H., Oh, S.-J., Kim, J.-S., 2014. Total utilization of waste tire rubber through pyrolysis to obtain oils and CO₂ activation of pyrolysis char. *Fuel Process. Technol.* 123, 57–64.

Clauzade, C., Osset, P., Hugrel, C., Chappert, A., Durande, M., Palluau, M., 2010. Life cycle assessment of nine recovery methods for end-of-life tyres. *Int. J. Life Cycle Assessment* 15, 883–892.

Corti, A., Lombardi, L., 2004. End life tyres: alternative final disposal processes compared by LCA. *Energy* 29, 2089–2108.

Cunliffe, A.M., Williams, P.T., 1998. Composition of oils derived from the batch pyrolysis of tyres. *J. Anal. Appl. Pyrol.* 44, 131–152.

Curran, T., Williams, I.D., 2012. A zero waste vision for industrial networks in Europe. *J. Hazard. Mater.* 207–208, 3–7.

de Marco Rodríguez, I., Laresgoiti, M.F., Cabrero, M.A., Torres, A., Chomón, M.J., Caballero, B., 2001. Pyrolysis of scrap tyres. *Fuel Process. Technol.* 72, 9–22.

DEPOTEC, 2011–2014. LIFE10 ENV/IE/000695, Depolymerisation Technology for Rubber with Energy Optimisation to Produce Carbon Products.

Díez, C., Martínez, O., Calvo, L.F., Cara, J., Morán, A., 2004. Pyrolysis of tyres. Influence of the final temperature of the process on emissions and the calorific value of the products recovered. *Waste Manage. (Oxford)* 24, 463–469.

Díez, C., Sánchez, M.E., Haxaire, P., Martínez, O., Morán, A., 2005. Pyrolysis of tyres: a comparison of the results from a fixed-bed laboratory reactor and a pilot plant (rotary reactor). *J. Anal. Appl. Pyrol.* 74, 254–258.

E.P.A., U.S., 1997. Air Emissions from Scrap Tire Combustion.

E.P.A., U.S., 1999. In-Use Marine Diesel Fuel.

E.U.-Directive, 1999. Council Directive 1999/31/EC of 26 April 1999 on the Landfill of Waste.

E.U.-Directive, 2008. DIRECTIVE 2008/98/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 19 November 2008 on Waste and Repealing Certain Directives.

E.U.-Directive, 2012. Directive 2012/33/EU of the European Parliament and of the Council of 21 November 2012 Amending Council Directive 1999/32/EC as Regards the Sulphur Content of Marine Fuels.

Edwin Raj, R., Robert Kennedy, Z., Pillai, B.C., 2013. Optimization of process parameters in flash pyrolysis of waste tyres to liquid and gaseous fuel in a fluidized bed reactor. *Energy Convers. Manage.* 67, 145–151.

EPD, 2011. Ministry of the Environment: A Technical Review of Municipal Solid Waste Thermal Treatment Practices: FINAL REPORT Stantec, Victoria, Canada.

ETRA, 1996. European Tyre Recycling Association.

ETRA, 2012. European Tyre Recycling Association 2012 Report.

ETRA, 2014. Annual Conference 2014, Pyrolysis Forum.

ETRMA, 1959. European Tyre & Rubber Manufacturing Association.

ETRMA, 2009. End of Life Tyre Guidance. Tyre Generic Exposure Scenario, Brussels, Belgium.

ETRMA, 2010. A Framework for Effective Management Systems, Brussels, Belgium.

- ETRMA, 2013a. Annual Report 2012–2013.
- ETRMA, 2013b. Statistics.
- EU-BREF, 2006. Reference Document on the Best Available Techniques for Waste Incineration.
- Eurostat, 2014. Labour Cost Index – Recent Trends.
- Fabbri, D., Vassura, I., 2006. Evaluating emission levels of polycyclic aromatic hydrocarbons from organic materials by analytical pyrolysis. *J. Anal. Appl. Pyrol.* 75, 150–158.
- Fink, J.K., 1999. Pyrolysis and combustion of polymer wastes in combination with metallurgical processes and the cement industry. *J. Anal. Appl. Pyrol.* 51, 239–252.
- Foo, K.Y., Hameed, B.H., 2010. Detoxification of pesticide waste via activated carbon adsorption process. *J. Hazard. Mater.* 175, 1–11.
- Freedonia-Study, 2013. Activated Carbon, US Industry Study with Forecasts for 2017 and 2022. Freedonia Group.
- Frigo, S., Seggiani, M., Puccini, M., Vitolo, S., 2014. Liquid fuel production from waste tyre pyrolysis and its utilisation in a diesel engine. *Fuel* 116, 399–408.
- Gabarrell, X., Font, M., Vicent, T., Caminal, G., Sarrà, M., Blánquez, P., 2012. A comparative life cycle assessment of two treatment technologies for the Grey Lanaset G textile dye: biodegradation by *Trametes versicolor* and granular activated carbon adsorption. *Int. J. Life Cycle Assessment* 17, 613–624.
- Gieré, R., Stille, P., 2004. Energy, Waste and the Environment: A Geochemical Perspective. Geological Society Publishing House.
- Graeff, A.G., Pilakoutas, K., Neocleous, K., Peres, M.V.N.N., 2012. Fatigue resistance and cracking mechanism of concrete pavements reinforced with recycled steel fibres recovered from post-consumer tyres. *Eng. Struct.* 45, 385–395.
- Gupta, V.K., Gupta, B., Rastogi, A., Agarwal, S., Nayak, A., 2011. Pesticides removal from waste water by activated carbon prepared from waste rubber tire. *Water Res.* 45, 4047–4055.
- Gupta, V.K., Ganjali, M.R., Nayak, A., Bhushan, B., Agarwal, S., 2012. Enhanced heavy metals removal and recovery by mesoporous adsorbent prepared from waste rubber tire. *Chem. Eng. J.* 197, 330–342.
- Gupta, V., Ali, I., Saleh, T., Siddiqui, M.N., Agarwal, S., 2013. Chromium removal from water by activated carbon developed from waste rubber tires. *Environ. Sci. Pollut. Res.* 20, 1261–1268.
- Gupta, V.K., Suhas, Nayak, A., Agarwal, S., Chaudhary, M., Tyagi, I., 2014. Removal of Ni (II) ions from water using scrap tire. *J. Mol. Liq.* 190, 215–222.
- Hajizadeh, Y., Onwudili, J.A., Williams, P.T., 2011. Removal potential of toxic 2378-substituted PCDD/F from incinerator flue gases by waste-derived activated carbons. *Waste Manage. (Oxford)* 31, 1194–1201.
- Haydary, J., Jelemenský, L., Gašparovič, L., Markoš, J., 2012. Influence of particle size and kinetic parameters on tire pyrolysis. *J. Anal. Appl. Pyrol.* 97, 73–79.
- Hjaila, K., Baccar, R., Sarrà, M., Gasol, C.M., Blánquez, P., 2013. Environmental impact associated with activated carbon preparation from olive-waste cake via life cycle assessment. *J. Environ. Manage.* 130, 242–247.
- Hofman, M., Pietrzak, R., 2011. Adsorbents obtained from waste tires for NO₂ removal under dry conditions at room temperature. *Chem. Eng. J.* 170, 202–208.
- Honus, S., Juchelkova, D., Campen, A., Wiltowski, T., 2014. Gaseous components from pyrolysis—characteristics, production and potential for energy utilization. *J. Anal. Appl. Pyrol.* 106, 1–8.
- Hu, H., Fang, Y., Liu, H., Yu, R., Luo, G., Li, A., Yao, H., 2014. The fate of sulfur during rapid pyrolysis of scrap tires. *Chemosphere* 97, 102–107.
- Huang, H., Tang, L., 2009. Pyrolysis treatment of waste tire powder in a capacitively coupled RF plasma reactor. *Energy Convers. Manage.* 50, 611–617.
- le, I.-R., Chen, W.-C., Yuan, C.-S., Hung, C.-H., Lin, Y.-C., Tsai, H.-H., Jen, Y.-S., 2012. Enhancing the adsorption of vapor-phase mercury chloride with an innovative composite sulfur-impregnated activated carbon. *J. Hazard. Mater.* 217–218, 43–50.
- Ioannidou, O., 2011. Activated Carbon Production from Agricultural Biomass and Their Use in the Removal Of Selected Pesticides, Phd Thesis of Chemical Engineering Department, Thessaloniki.
- Ioannidou, O., Zabaniotou, A., 2007. Agricultural residues as precursors for activated carbon production—a review. *Renew. Sust. Energy Rev.* 11, 1966–2005.
- Islam, M.R., Joardder, M.U.H., Hasan, S.M., Takai, K., Haniu, H., 2011. Feasibility study for thermal treatment of solid tire wastes in Bangladesh by using pyrolysis technology. *Waste Manage. (Oxford)* 31, 2142–2149.
- Islam, M.R., Islam, M.N., Mustafa, N., Rahim, M.A., Haniu, H., 2013. Thermal recycling of solid tire wastes for alternative liquid fuel: the first commercial step in Bangladesh. *Proc. Eng.* 56, 573–582.
- Kebritchi, A., Firoozifar, H., Shams, K., Jalali-Arani, A., 2013. Effect of pre-devulcanization and temperature on physical and chemical properties of waste tire pyrolytic oil residue. *Fuel* 112, 319–325.
- Laresgoiti, M.F., Caballero, B.M., de Marco, I., Torres, A., Cabrero, M.A., Chomón, M.J., 2004. Characterization of the liquid products obtained in tyre pyrolysis. *J. Anal. Appl. Pyrol.* 71, 917–934.
- Li, L., Liu, S., Zhu, T., 2010a. Application of activated carbon derived from scrap tires for adsorption of Rhodamine B. *J. Environ. Sci.* 22, 1273–1280.
- Li, X., Xu, H., Gao, Y., Tao, Y., 2010b. Comparison of end-of-life tire treatment technologies: a Chinese case study. *Waste Manage. (Oxford)* 30, 2235–2246.
- Lopez, G., Aguado, R., Olazar, M., Arabiourrutia, M., Bilbao, J., 2009. Kinetics of scrap tyre pyrolysis under vacuum conditions. *Waste Manage. (Oxford)* 29, 2649–2655.
- López, F.A., Centeno, T.A., Alguacil, F.J., Lobato, B., Urien, A., 2013. The GRAUTHERMIC-Tyres process for the recycling of granulated scrap tyres. *J. Anal. Appl. Pyrol.* 103, 207–215.
- Marsh, H., Reinoso, F.R., 2006. Activated Carbon, first ed. Elsevier Science, Oxford, UK.
- Martínez, J.D., Murillo, R., García, T., Veses, A., 2013a. Demonstration of the waste tyre pyrolysis process on pilot scale in a continuous auger reactor. *J. Hazard. Mater.* 261, 637–645.
- Martínez, J.D., Puy, N., Murillo, R., García, T., Navarro, M.V., Mastral, A.M., 2013b. Waste tyre pyrolysis – a review. *Renew. Sust. Energy Rev.* 23, 179–213.
- Martínez, J.D., Rodríguez-Fernández, J., Sánchez-Valdepeñas, J., Murillo, R., García, T., 2014. Performance and emissions of an automotive diesel engine using a tire pyrolysis liquid blend. *Fuel* 115, 490–499.
- Mastral, A.M., Murillo, R., Callen, M.S., Garcia, T., 2000. Optimisation of scrap automotive tyres recycling into valuable liquid fuels. *Resour. Conserv. Recycl.* 29, 263–272.
- Mui, E.L.K., Ko, D.C.K., McKay, G., 2004. Production of active carbons from waste tyres—a review. *Carbon* 42, 2789–2805.
- Mui, E.L.K., Cheung, W.H., Valix, M., McKay, G., 2010. Mesoporous activated carbon from waste tyre rubber for dye removal from effluents. *Micropor. Mesopor. Mater.* 130, 287–294.
- Papakonstantinou, C.G., Tobolski, M.J., 2006. Use of waste tire steel beads in Portland cement concrete. *Cement Concrete Res.* 36, 1686–1691.
- PAS-107, 2012. Specification for the manufacture and storage of size reduced tyre materials. European Committee for Standardization.
- Peters, M.S., Timmerhaus, K.D., West, R.E., Timmerhaus, K., West, R., 1968. Plant Design and Economics for Chemical Engineers. McGraw-Hill, New York.
- REACH, 2006. REACH Directive. In: EU (Ed.).
- RMA, 2009. U.S. Scrap Tire Market Summary.
- Roy, C., Rastegar, A., Kaliaguine, S., Darmstadt, H., Tochev, V., 1995. Physicochemical properties of carbon blacks from vacuum pyrolysis of used tires. *Plast. Rub. Compos. Process. Appl.* 23, 21–30.
- Saleh, T.A., Gupta, V.K., Al-Saadi, A.A., 2013. Adsorption of lead ions from aqueous solution using porous carbon derived from rubber tires: experimental and computational study. *J. Colloid Interface Sci.* 396, 264–269.
- Samolada, M.C., Zabaniotou, A.A., 2012. Potential application of pyrolysis for the effective valorisation of the end of life tires in Greece. *Environ. Dev.* 4, 73–87.
- Shah, J., Jan, M.R., Mabood, F., 2009. Recovery of value-added products from the catalytic pyrolysis of waste tyre. *Energy Convers. Manage.* 50, 991–994.
- Sienkiewicz, M., Kucinska-Lipka, J., Janik, H., Balas, A., 2012. Progress in used tyres management in the European Union: a review. *Waste Manage. (Oxford)* 32, 1742–1751.
- Skodras, G., Diamantopoulou, I., Zabaniotou, A., Stavropoulos, G., Sakellaropoulos, G.P., 2007. Enhanced mercury adsorption in activated carbons from biomass materials and waste tires. *Fuel Process. Technol.* 88, 749–758.
- Stavropoulos, G.G., 2005. Precursor materials suitability for super activated carbons production. *Fuel Process. Technol.* 86, 1165–1173.
- Stavropoulos, G.G., Zabaniotou, A.A., 2009. Minimizing activated carbons production cost. *Fuel Process. Technol.* 90, 952–957.
- Tanthapanichakoon, W., Ariyadejwanich, P., Japthong, P., Nakagawa, K., Mukai, S.R., Tamon, H., 2005. Adsorption-desorption characteristics of phenol and reactive dyes from aqueous solution on mesoporous activated carbon prepared from waste tires. *Water Res.* 39, 1347–1353.
- TRA, 2012. Specification for the manufacture and storage of size reduced tyre materials. Tyre Recovery Association.
- Troca-Torrado, C., Alexandre-Franco, M., Fernández-González, C., Alfaro-Domínguez, M., Gómez-Serrano, V., 2011. Development of adsorbents from used tire rubber: their use in the adsorption of organic and inorganic solutes in aqueous solution. *Fuel Process. Technol.* 92, 206–212.
- UNI-CEN/TS-14243, 2010. Materials produced from end of life tyres – specification of categories based on their dimension(s) and impurities and methods for determining their dimension(s) and impurities. European Committee for Standardization.
- Uruburu, Á., Ponce-Cueto, E., Cobo-Benita, J.R., Ordieres-Meré, J., 2013. The new challenges of end-of-life tyres management systems: a Spanish case study. *Waste Manage. (Oxford)* 33, 679–688.
- WFD, 2008. Waste Framework Directive.
- WID, 2008. Waste Incineration Directive.
- Williams, P.T., 2013. Pyrolysis of waste tyres: a review. *Waste Manage. (Oxford)* 33, 1714–1728.
- Williams, P.T., Brindle, A.J., 2003. Aromatic chemicals from the catalytic pyrolysis of scrap tyres. *J. Anal. Appl. Pyrol.* 67, 143–164.
- Wilts, H., Dehoust, G., Jepsen, D., Knappe, F., 2013. Eco-innovations for waste prevention—best practices, drivers and barriers. *Sci. Total Environ.* 461–462, 823–829.
- WRAP, 2009. Protocol for Tyre Derived Rubber Materials.
- Zabaniotou, A.A., Stavropoulos, G., 2003. Pyrolysis of used automobile tires and residual char utilization. *J. Anal. Appl. Pyrol.* 70, 711–722.
- Zabaniotou, A., Madau, P., Oudenne, P.D., Jung, C.G., Delplancke, M.P., Fontana, A., 2004. Active carbon production from used tire in two-stage procedure: industrial pyrolysis and bench scale activation with H₂O–CO₂ mixture. *J. Anal. Appl. Pyrol.* 72, 289–297.